

Chlorinated Alcohols: II. The Chlorination of Oleyl Alcohol

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Abstract

Chlorination of oleyl alcohol gives mainly 9,10-dichlorostearyl alcohol but a variety of other products are also formed. By-products include 9(10)-(9,10-dichlorostearoxy)-10(9)-chlorostearyl alcohol (14%) and 9,10-dichlorostearyl 9,10-dichlorostearate (3-4%) in addition to three or four less clearly defined products (12%). One group of products is apparently derived from participation of the hydroxyl group in the chlorine addition step while the other products formed by the reaction of the hydroxyl group with chlorine or chlorine and hydrogen chloride.

Introduction

CHLORINATED FATTY ALCOHOLS have been of interest because they can be converted to the sodium dichloroalkyl sulfate detergents. Earlier work showed the additive chlorination of oleyl alcohol, sulfation, and detergency (9). The product, considered to be 9,10-dichlorostearyl alcohol and formed in quantitative yield as a colorless oil with reasonable analysis for chlorine, has been found by TLC to contain at least four components (1). The present work was undertaken to identify the by-products that occur upon the chlorination of oleyl alcohol, and to determine how they are formed.

Experimental Procedures

The oleyl alcohol used in this work was prepared by distillation of two commercial oleyl alcohols, Novol (Kroda) and Adol 90 (Ashland), on a 40-plate spinning band column. The alcohols obtained were from 95-98% oleyl alcohols containing from 1-3% stearyl alcohol and from 0.2-0.5% acidic material considered as oleic acid.

Reference compounds were collected and used to help identify components of the chlorination mixture. Methyl 9,10-dichlorostearate was prepared by chlorination of methyl oleate (5). Methyl 9(10)-methoxy-10(9)-chlorostearate was prepared by chlorination of oleic acid in methanol (6). A commercial sample of stearyl alcohol (98+%) was used without further purification.

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9,10,12,13-Tetrachlorostearyl Alcohol

Linoleic acid (90%) was chlorinated according to a procedure described by Lyness and Quackenbush (5) to produce a yellow paste. This crude material was reduced with diborane (2), producing tetrachlorostearyl alcohol as a paste, and then recrystallized from Skelly B several times to obtain a low yield of white solid, mp 105.5-106.5 C, homogeneous by TLC (benzene-ether, 75:25).

Analysis. Calculated for $C_{18}H_{34}Cl_4O$: C, 52.95; H, 8.40; Cl, 34.73. Found: C, 53.16; H, 8.41; Cl, 35.03.

A strong infrared absorption at 3300 cm^{-1} indicated the presence of the hydroxyl group.

The mother liquor from the above room temperature recrystallization was cooled to -25 C and the resulting small amount of precipitate was removed. Decolorization with charcoal and concentration under vacuum resulted in a pale yellow oil. After purification by preparative TLC the material was still an oil.

9,10-Dichlorostearyl 9,10-Dichlorostearate

9,10-Dichlorostearic acid was prepared by -15 C chlorination of oleic acid in methylene chloride. The crude product was recrystallized from Skelly B to obtain a material at mp $36.5-38\text{ C}$ (5). This acid (5 g, 0.0137 mole) was dissolved in Skelly B (20 ml) and mixed with thionyl chloride (1.71 g, 0.0144 mole). The mixture was heated to reflux for 24 hrs. It was then concentrated under vacuum, producing 9,10-dichlorostearoyl chloride, and used without further purification. The acyl chloride was dissolved in Skelly B (30 ml), mixed with 9,10-dichlorostearyl alcohol (4.65 g, 0.014 mole) and pyridine (1.08 g, 0.014 mole), and the mixture was heated under reflux for 1.5 hr. The product was washed with water, dried (MgSO_4) and concentrated under vacuum to a pale yellow oil with a strong absorption, at 1735 cm^{-1}

$$\begin{array}{c} \text{O} \\ || \\ (\text{R}-\text{C}-\text{O}-\text{R}), \end{array}$$
in the infrared spectrum.

Chlorination Procedures

The chlorination procedure was essentially that described in an earlier report (9). The details of our experiments are described in Table I.

Isolation and Identification

By comparing the infrared spectra of the reference compounds we were able to assign certain absorptions to certain structural features in these compounds. The following list describes these correlations.

TABLE I
Effect of Temperature on Oleyl Alcohol Chlorination^{a,b}

Expt.	Reaction temp.	Exotherm	% Cl	I.V.	Percentage upon distillation (approx.) ^c		
					Stearyl alcohol	Dichlorostearyl alcohol	Residue ^d
Theory			21.0	0.0			0.0
1	-13C	3C	20.4	0.2	1	70	26
2	-3	5	19.9	0.3	1.4	70	17
3	+6	6	20.0	0.5	1.8	72*	26*
4	+17	7	19.8	0.6
5	+26	6	19.6	0.6	2.5	58	28

^a Oleyl alcohol (50 g) in methylene chloride (175 ml).

^b Yields were consistent from 99-100% of theory.

^c TLC of the various fractions indicates that only very small amounts of new products form during distillation.

^d Dichlorostearyl alcohol distills from 160-175 C/0.05 mm; the residue is material not distilling at 205 C/0.05 mm. The fraction collected between these ranges appears to be mainly 9,10-dichlorostearyl alcohol.

* Yields based on column chromatography of the sample (silica gel, benzene-ether, 75:25). Residue is considered TLC spots 2, 3 and 4.

Structural Feature	Frequency (cm ⁻¹)
RCH ₂ OH	3340 and 1060
R-CH-O-CH ₃	1100 and
R-CH-Cl	685
R-CH-Cl	
R-CH-Cl	650
-(CH ₂) _n	725

Thin-layer chromatography of the chlorinated oleyl alcohols was run on silica gel plates with benzene-ether (75:25) as an eluant. In this solvent system, four components were observed and arbitrarily numbered 1 through 4. The R_f values and numbers are: TLC 1, $R_f = 0.27$; TLC 2, $R_f = 0.39$; TLC 3, $R_f = 0.47$, and TLC 4, $R_f = 0.8$. The components were separated and purified mainly by preparative TLC, although component 4, because of its fast migration rate, was purified by a combination of column chromatography (benzene-ether, 75:25) and preparative TLC. Infrared spectra were run on a Perkin-Elmer 237-B; NMR were run on a Varian A-60 spectrometer.

Relative amounts of each component were obtained by distillation (see Table I); however, to double check these numbers we subjected a typical sample to column chromatography. All fractions were analyzed by TLC and amounts of each component were estimated and combined. On this sample (Table I, Experiment 3) the relative amounts were TLC 1, 74%; TLC 2, 14%; TLC 3, 3%; and TLC 4, 9%. In the solvent system (mainly benzene-ether, 75:25) we used stearyl alcohol; 9,10-dichlorostearyl alcohol and 9,10,12,13-tetrachlorostearyl alcohol were indistinguishable, i.e., they had similar R_f values. Presumably polychloroalcohols from substitution reactions would also escape detection by TLC. However, the agreement in the yield of 9,10-dichlorostearyl alcohol by distillation and chromatography and also the per cent chlorine in the crude reaction mixtures suggest that the polychloro alcohol content of the samples is quite low. Listed below is the information accumulated on each component.

TLC Spot 1

This component was easily separable by preparative TLC but was more conveniently purified by simple vacuum distillation. When carefully distilled, the product was a colorless oil containing only a trace of stearyl alcohol (VPC, $\frac{1}{4}$ in. by 4 ft, OV-1 column) and only one major component. The NMR spectrum with absorptions at δ 0.86–2.1 ppm (several absorptions, 31.3, CH₃(CH₂)₇CC(CH₂)₇C-O), 2.74 ppm (singlet, 1.00, C-O-H), 3.51 ppm (triplet, 1.95, -CH₂O), 3.92 ppm (complex, 1.95, -CHClCHCl-) and the infrared spectrum with absorptions at 3340 and 1060 cm⁻¹ (OH), 725 cm⁻¹ -(CH₂)_n and 650 cm⁻¹ (-CHClCHCl-) show that this material is 9,10-dichlorostearyl alcohol.

Analysis. Calculated for C₁₈H₃₆OCl₂: Cl, 20.89. Found: Cl, 21.04.

TLC Spot 2

Distillation of chlorinated oleyl alcohol results in the accumulation of components 2, 3 and 4 in the pot residue. Pure identical samples were obtained by preparative TLC of both the chlorinated alcohol and the pot residue. The infrared spectrum has absorptions at 3350 and 1060 cm⁻¹ (CH₂OH), 1100

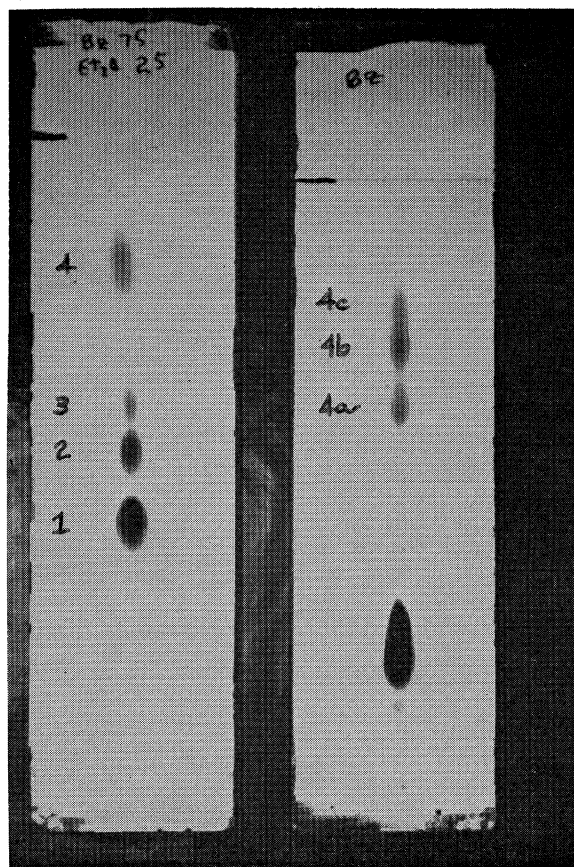


Fig. 1. TLC plates of a chlorinated oleyl alcohol sample showing (left) TLC spots 1, 2, 3 and 4 and (right) TLC spots 4a, 4b and 4c.

cm⁻¹ (R-O-CH₂R), 725 cm⁻¹ -(CH₂)_n-, 685 cm⁻¹ (-CHClCHOR-) and 650 cm⁻¹ (-CHClCHCl-). The NMR spectrum showed many superimposed absorptions so the trichloroacetylurethane derivative was prepared. The spectrum of the derivative had absorptions at δ 0.85–2.1 ppm (several absorptions, 62.2) 3.1–3.6 ppm (multiplet, 3.0), 3.6–4.35 ppm (multiplet, 4.8) and 8.2 ppm (singlet, 0.8, -O-CNHCCCl₃). The structure that best fits the



data is that of 9(10)-(9,10-dichlorostearyloxy)-10(9)-chlorostearyl alcohol.

TLC Spot 3

The component of TLC spot 3 was not entirely purified. The sample was mainly spot 3 but another compound moving slightly faster than spot 3 was observed. This compound was called 3a. In addition, the sample was also contaminated with a small amount of TLC spot 2. The infrared spectrum of this material has absorptions at 3400 and 1060 cm⁻¹ (shoulder) (CH₂OH), a very intense band at 1100 cm⁻¹ (R₃C-OCH₂R), 725 cm⁻¹ -(CH₂)_n-, 685 cm⁻¹ (-CHClCHOR-) and 650 cm⁻¹ (-CHClCHCl-). The spectrum is superimposable on that of TLC spot 2 except that the band at 1100 cm⁻¹ is relatively more intense than the band at 1060 cm⁻¹. Also, the absorption at 685 cm⁻¹ is relatively more intense than the absorption at 650 cm⁻¹. The yield of this material (ca. 3%) and the infrared data as well as its position on the TLC plate lead us to speculate that this material is the trimeric chloroether, the next higher homolog of TLC component 2.

TLC Spot 4

In benzene, TLC of this spot shows that it actually contains three materials which we designate 4a, 4b and 4c. Material 4a has the lowest R_f value while 4c has the highest. The relative concentration of these components is estimated to be about 3:4:2 for a total concentration of about 9%. Each of these components was prepared in pure form.

The infrared spectrum of 4a has absorptions at 1735 cm^{-1} (ester), 725 cm^{-1} ($-(\text{CH}_2)_n-$) and 650 cm^{-1} ($-\text{CHClCHCl}-$) but no hydroxyl absorptions. The infrared spectrum of 9,10-dichlorostearyl 9,10-dichlorostearate had been run earlier and was identical to that of 4a. In addition, the TLC behavior in several solvents (benzene, Skelly B-acetone, 95:5, ethanol) of 4a was identical with that of the ester. The NMR spectrum was run and the reference ester has absorptions at δ 0.8–2.5 ppm and at 3.85–4.25 ppm but these are both complex. The NMR spectrum of 4a was identical.

Component 4b has the following characteristics: the infrared spectrum has no hydroxyl and no carbonyl but it does show absorptions at 650 cm^{-1} ($-\text{CHClCHCl}-$) and has bands at 1070 and 1125 cm^{-1} with the 1125 cm^{-1} band the stronger of the two. The NMR spectrum of this material is poorly resolved but bands appear from $\delta\ 0.7\text{--}2.1\text{ ppm}$ (21), $3.2\text{--}3.75\text{ ppm}$ (1.0) and $3.75\text{--}4.25\text{ ppm}$ (1.0). There appear to be no absorptions in the vinyl region.

Component 4c has properties very similar to 4b except that in the infrared spectrum the band at 1070 cm^{-1} is stronger than the band at 1125 cm^{-1} . The NMR spectrum is nearly identical with that of 4b.

Action of Chlorine on 9,10-Dichlorostearyl Alcohol

A sample of distilled 9,10-dichlorostearyl alcohol (2 g) was dissolved in methylene chloride (10 g) and the solution cooled in a -30 C methanol-ice bath. Chlorine gas was bubbled through the solution briefly until it was the usual yellow-green color. The flask was then stoppered and allowed to stand at -30 C for 30 min. The reaction mixture was then concentrated under vacuum to give a nearly colorless oil. TLC shows this sample to be considerably enriched in TLC Spot 4a (9,10-dichlorostearyl 9,10-dichlorostearate). Preparative TLC shows that a considerable amount of 4b is also produced by this treatment.

Action of Chlorine and Hydrogen Chloride on 9,10-Dichlorostearyl Alcohol

The alcohol (1 g) in methylene chloride (5 ml) was treated with chlorine and then hydrogen chloride and allowed to stand 30 min at room temperature. Preparative TLC of this product showed that 4c was the major new component. In addition, some 4a and probably 4b were also formed.

Action of Hydrogen Chloride on 9,10-Dichlorostearyl Alcohol

The alcohol (1 g) in methylene chloride (5 ml) was cooled to -30°C , saturated with hydrogen chloride and stored for 20 min. Concentration under vacuum gave a yellow oil that, upon TLC, was unchanged from the starting alcohol.

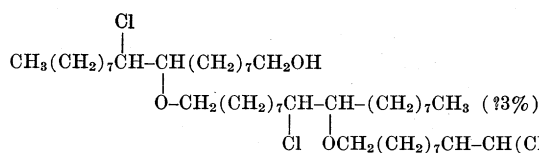
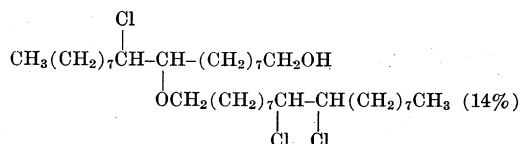
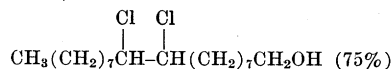
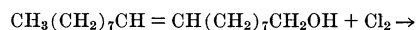
Action of Chlorine on 9,10-Dichlorostearyl Alcohol

The alcohol (1 g) in methylene chloride (5 g) was saturated with chlorine at room temperature and the reaction vessel was stoppered. An exotherm was noted and bubbles of gas were formed as the solution

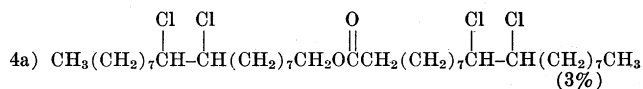
became colorless. The reaction mixture was concentrated on a rotary evaporator to a colorless oil. TLC showed the main component to be 4c but some 4a was also formed.

Discussion

This work shows that chlorination of oleyl alcohol in methylene chloride (50 g/175 ml, 6 C) gives at least six different products, some of which are shown below.



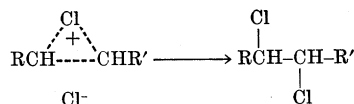
plus positional isomers



4b and 4c) Unidentified, 4% and 2%.

Variations in the temperature of chlorination do not serve to eliminate the formation of any component. In fact, TLC of all of the chlorination mixtures shows that, at least for our temperature range, they are all similar. The relatively low yield of 9,10-dichlorostearyl alcohol observed in Experiment 5 (+26 C) may be indicating the upper limits for this chlorination, however. Surprisingly no trace of olefinic hydrogen in any of the components of the sample chlorinated at +6 C was found. Chlorinated elaidyl alcohol also has a TLC spectrum similar to that of chlorinated oleyl alcohol, strongly suggesting that the use of a *cis* or *trans* olefin makes little difference in the kind of products formed.

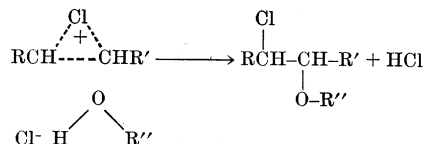
The main product from the chlorination of oleyl alcohol is 9,10-dichlorostearyl alcohol, TLC spot 1. Additive chlorination of symmetrical internal olefins is usually considered (7) to be a heterolytic reaction involving initial attack of a chloronium ion and subsequent *trans* attack of a chloride ion. Because the addition is *trans* and the substrate is



unsymmetrical, the reaction product is a pair of enantiomers. Pure samples of 9,10-dichlorostearyl alcohol are perhaps best obtained by fractional distillation under a good vacuum. The only component of the reaction mixture that is more volatile is stearyl alcohol and the rest of the mixture appears to be much less volatile.

TLC spot 2 is apparently formed because the hydroxyl group of the oleyl or 9,10-dichlorostearyl alcohol competes with the chloride ion in attack of

the alkylchloronium ion. Chlorinations run in participating



solvents such as alcohols result in the formation of β -chloro ethers as the main products. For example, Hennion and Irwin (4) found that chlorination of 3-hexene in 4 moles of methanol gave the chloro ether as 65% of the reaction product. Chlorination of oleic acid in an excess of methanol or *sec*-butyl alcohol is also reported (6) to give mainly the chloro ethers. Since chlorination of oleyl alcohol essentially amounts to chlorination of an olefin in the presence of an equimolar concentration of a participating solvent, the formation of the chloro ether is not surprising.

TLC spot 3 could not be purified completely; however, we did get a sample that appears to be about half TLC spot 3 and then about equal amounts of component 2 and a new component which we called TLC spot 3a. Component 3a has a slightly higher R_f value than component 3. The infrared spectrum of this enriched sample is identical with the spectrum of component 2 except that the ether bands are stronger relative to the hydroxyl bands. We suggest that this compound has structure 3 and speculate that TLC spot 3a, which appears only when 3 is concentrated, is the tetramer corresponding to compound 3. Speculation is based on the fact that the dimer, trimer, etc., that are formed, should be able to participate in subsequent chlorinations to give trimers, tetramers, etc., by virtue of the remaining free hydroxyl group. Since the amount of the n^{th} telomer formed is only about one fifth of the $(n-1)^{\text{th}}$ telomer formed, the concentration of trimer, tetramer, etc., in the reaction mixture, should be quite low. Treatment of purified 9,10-dichlorostearyl alcohol with chlorine or chlorine and hydrogen chloride does not give rise to TLC spots 2 and 3.

While components 1, 2 and probably 3 arise from additive chlorination of the double bond and from

hydroxyl participation in that addition, components 4a, 4b and 4c are generated by reaction of the primary alcohol function with chlorine or chlorine-hydrogen chloride mixtures. For example, we find that treatment of purified 9,10-dichlorostearyl alcohol with chlorine at -30°C results mainly in the formation of 4a and 4b. At room temperature, however, similar treatment, or treatment with chlorine and hydrogen chloride, appears to give mainly 4c along with some 4a. We have found that compound 4a is 9,10-dichlorostearyl 9,10-dichlorostearate. In the chlorinated oleyl alcohol prepared, ca. 0.2–0.5% of the 9,10-dichlorostearyl 9,10-dichlorostearate probably came from oleic acid present in the oleyl alcohol. However, the main part of this component (ca. 3%) must be formed by excess elemental chlorine present during and at the end of chlorination. The steps involved in this oxidation are not clear but chlorination of alcohols is reported (8) to give aldehydes via the α -chloro alcohol and chlorination of aldehydes such as propanal is reported to produce (3) carboxylic acids in good yields.

Components 4b and 4c have not been identified. The infrared absorptions show the absence of hydroxyl or carbonyl but 4b and 4c do contain *vic*-chlorine and have absorptions at 1070 and 1125 cm^{-1} that suggest some sort of ether linkage. The NMR spectra are nearly identical and seem to be consistent with the infrared spectra.

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